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A joint model-based experimental design approach for the identification of kinetic models in continuous flow laboratory reactors

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ABSTRACT

Continuous flow laboratory reactors are typically used for the development of kinetic models for catalytic reactions. Sequential model-based design of experiments (MBDoE) procedures have been proposed in literature where experiments are optimally designed for discriminating amongst candidate models or for improving the estimation of kinetic parameters. However, the effectiveness of these procedures is strongly affected by the initial model uncertainty, leading to suboptimal design solutions and higher number of experiments to be executed. A joint model-based design of experiments (j-MBDoE) technique, based on multi-objective optimization, is proposed in this paper for the simultaneous solution of the dual problem of discriminating among competitive kinetic models and improving the estimation of the model parameters. The effectiveness of the proposed design methodology is tested and discussed through a simulated case study for the identification of kinetic models of methanol oxidation over silver catalyst.

1. Introduction

Model-based design of experiments (MBDoE) techniques represent a consolidated tool for the rapid assessment and identification of fundamental kinetic models by optimally designing a set of experiments yielding the most informative data to be used for model identification (Franceschini and Macchietto, 2008). As per conventional model building procedures (Asprey and Macchietto, 2002; Blau et al., 2008), experiments are optimally designed with the following purposes: *i*) discriminating between structurally identifiable candidate models, in order to identify the most suitable model structure representing a system (Hunter and Reiner, 1965; Buzzi-Ferraris and Forzatti, 1983, 1984; Schwaab et al., 2006); *ii*) improving the precision of parameter estimates, once a suitable model structure is determined (Galvanin et al., 2007; Bandara et al., 2009). Whilst the first objective is achieved based on the maximisation of the discriminating power (i.e. a function for quantitatively evaluating the deviation between model predictions), the second is based on the maximisation of the expected information, given as a measurement function of the Fisher Information Matrix (FIM), allowing to increase the confidence on parameter estimation. The sequential iteration of steps *i*) (MBDoE for model discrimination) and *ii*) (MBDoE for improving parameter precision) leads to the detection of the best model structure and to a statistically reliable estimation of the model parameters, minimising the experimental trials required by the model identification task. This optimal design approach has been recently applied also to the design of steady-state (Reizman and Jensen, 2012) as well as transient experiments (Schaber et al., 2014) for the development of kinetic models in microfluidic devices, underlining the potential of MBDoE techniques in the identification of reaction kinetics. Nevertheless, the conventional sequential MBDoE approach used for model building is affected by several limitations due to the intrinsic nature of the optimal design problem. In fact, at the beginning of the MBDoE procedure, when both the model structure and the set of model parameters are unknown, the design for model discrimination could be highly ineffective for discriminating amongst candidate kinetic models when the optimally designed experimental conditions are applied to the actual system. Furthermore, due to model uncertainty, the planned discriminating experiments could provide a very low level of information for the estimation of the kinetic parameters, and this fact could severely affect the reliability of model predictions. Finally, the need of *sequentially* performing the design for model discrimination and the design for improving parameter precision procedures leads to the execution of a large number of experiments for obtaining reliable kinetics, prolonging time and effort required by the entire modelling activity.

In order to overcome these issues, Hill et al., 1968 introduced the concept of joint experimental design, i.e. a design for both establishing the form of an adequate model representing a system (i.e. the model structure) and to obtain a precise estimation of its set of parameters. A multi-objective design criterion was proposed and

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Nomenclature

General symbols

AIC	Akaike information criterion
c_i	Species concentration [mol/m3]
D	Design space
F	Flow rate [mL/min]
N	Number of experimental points
N_{exp}	Number of experiments
N^M	Number of candidate models
N^{reaz}	Number of reactions
n_{sp}	Number of sampling points
N_x	Number of state variables
N_y	Number of measured responses
N_θ	Number of parameters
n_φ	Number of design variables
P	Pressure [bar]
P_i^0	Preliminary probability of the i-th model to be the "true" model
P_i	Probability of the i-th model to be the "true" model
RFI_{ij}	Relative Fisher information of the i-th experiment for the j-th model
r_j	Rate of the j-th reaction
s_{ij}	ij-th element of the $Ny \times Ny$ matrix of measurement error
t	Time [s]
t_i^{sw}	i-th switching time
T	Temperature [K]
t_i	t-value for the i-th model paramater
v_z	Speed of fluid flow [m/s]
v_i^θ	Variance of the i-th model parameter
y_i	i-th measured response
$\hat{y}_i$	i-th predicted response
$w_{M,N}^{MD}$	MN-th element of the selection matrix $\mathbf{W}^{\mathrm{MD}}$ for model discrimination
w_j^{PE}	j-th element of vector $\mathbf{W}^{\mathrm{PE}}$ for improving parameter estimation
z	Axial coordinate [m]

Vectors and Matrices [dimension]

$\mathbf{H}_\theta$	Dynamic information matrix $[N_\theta \times N_\theta]$
$\mathbf{H}_\theta^0$	Preliminary information matrix $[N_\theta \times N_\theta]$
$\mathbf{t}^{sp}$	Vector of sampling points $[n_{sp}]$
$\mathbf{y}$	Measurements vector $[N_y]$
$\hat{\mathbf{y}}$	Vector of estimated responses $[N_y]$
y^0	Vector of initial conditions on measured variables $[N_y]$
$\mathbf{u}$	Vector of manipulated inputs $[N_u]$
$\mathbf{V}_\theta$	Variance-covariance matrix of model parameters $[N_\theta \times N_\theta]$
u	Vector of manipulated inputs $[N_u]$
$\mathbf{V}_\theta$	Variance-covariance matrix of model parameters $[N_\theta \times N_\theta]$
$\mathbf{x}$	Vector of state variables $[N_x]$
$\mathbf{x}^0$	Vector of initial states $[N_x]$
$\dot{\mathbf{x}}$	Vector of derivatives on state variables $[N_x]$
φ	Design vector $[n_\varphi]$
$\boldsymbol{\varphi}^{\mathrm{opt}}$	Optimal design vector $[n_\varphi]$
$\boldsymbol{\varphi}^{\mathrm{MD}}$	Optimal design vector for model discrimination $[n_\varphi]$
$\boldsymbol{\varphi}^{\mathrm{PE}}$	Optimal design vector for improving parameter estimation $[n_\varphi]$
$\boldsymbol{\varphi}^{JD}$	Optimal design vector for joint design $[n_\varphi]$
$\boldsymbol{\theta}$	Vector of values of true model parameters for the subject/system $[N_{\boldsymbol{\theta}}]$
$\hat{\theta}$	Vector of estimated values of model parameters $[N_{\boldsymbol{\theta}}]$
$\hat{\theta}^0$	Vector of preliminary estimated values of model parameters $[N_{\boldsymbol{\theta}}]$
$\mathbf{W}^{\mathrm{MD}}$	Selection matrix for model discrimination $[NM \times NM]$
$\mathbf{W}^{\mathrm{PE}}$	Selection vector for improving parameter estimation $[N^M]$

Greek letters

Δ_i	i-th transient time between consecutive experiments
σ_{yi}	Standard deviation of the i-th measured response
ν_{ij}	Stoichiometric coefficient of the$i$-th species in the j-th reaction
$\boldsymbol{\theta}_i$	i-th model parameter
τ	Experiment duration
ψ	$\mathbf{V}_{\boldsymbol{\theta}}$ measurement function (design criterion)
χ_i^2	Chi-square statistics
χ_{Ref}^2	Reference chi-square
Ψ^{MD}	Design objective function for model discrimination (discriminating power)
Ψ^{PE}	Design objective function for improving parameter estimation
ε	Epsilon variable for multi-objective j-MBDoE formulation
$\varepsilon^{\mathrm{MIN}}$	Minimum epsilon value
$\varepsilon^{\mathrm{MAX}}$	Maximum epsilon value

Acronyms

AIC	Akaike information criterion
DAEs	Differential and algebraic equations system
FIM	Fisher information matrix
j-MBDoE	Joint model-Based design of experiments
MBDoE	Model-based design of experiments
MD	Model discrimination
NLP	Nonlinear programming problem
PE	Parameter estimation
PFR	Plug flow reactor
SQP	Sequential quadratic programming

applied to several case studies over a predefined grid of experimental design points. More recently Petrov et al. (1991) and Akiti et al. (1997) applied a joint design approach for the investigation of reaction kinetics. However, in both studies the design objective functions were evaluated on a grid of experimental conditions and no direct multi-objective optimisation algorithm was applied for the design of the optimal experimental conditions.

In this paper, a joint model-based design of experiments (j-MBDoE) procedure is proposed for the development of kinetic models for simultaneously discriminating amongst candidate kinetic models and improving the estimation of kinetic parameters. Preliminary data from the reactors is used for model discrimination and to screen the most informative regions of the design space. According to j-MBDoE, trade-off solutions between metrics of Fisher information and discriminating power are computed using a multi-objective optimisation algorithm and are used to design a sequence of steady-state experiments. The effectiveness of the proposed design strategy is tested and critically discussed through a case study for the identification of kinetic models of methanol oxidation over silver catalyst, where the effectiveness of different optimal design configurations is compared and quantitatively assessed. The rest of the paper is organised as follows.